

PATENT APPLICATION

Alfred W. Mak, a citizen of the United States, residing at
32722 Fellows Court
Union City, California 94587

Mei Chang, a citizen of the United States, residing at
12881 Corte de Arguello
Saratoga, California 95070

Jeong Soo Byun, a citizen of South Korea, residing at,
20975 Valley Green Drive #257
Cupertino, California 95014

Hua Chung, a citizen of Taiwan, Republic of China, residing at,
4645 Piper Drive
San Jose, California 95129

Ashok Sinha, a citizen of the United States, residing at,
4176 Hubbart Dr.
Palo Alto, California 94306

Moris Kori, a citizen of the United States, residing at,
55 Hamilton Court
Palo Alto, California 94301

Applied Materials, Inc.
3050 Bowers Avenue
Santa Clara, California 95054
A Delaware Corporation

Entity: Large

PATENT COUNSEL
APPLIED MATERIALS, INC.
Legal Affairs Department
P.O. Box 1450A
Santa Clara, CA 95052
Tel: 512 527-0104

SYSTEM AND METHOD TO FORM A COMPOSITE FILM STACK UTILIZING SEQUENTIAL DEPOSITION TECHNIQUES

BACKGROUND OF THE INVENTION

This invention relates to the processing of semiconductor substrates. More particularly, this invention relates to improvements in the process of forming contacts.

Formation of contacts in multi-level integrated circuits poses many challenges to the semiconductor industry as the drive to increase circuit density continues, due to the reduction in size of the circuit features. Contacts are formed by depositing conductive interconnect material in an opening on the surface of insulating material disposed between two spaced-apart conductive layers. The aspect ratio of such an opening inhibits deposition of conductive interconnect material that demonstrates satisfactory step coverage and gap-fill, employing traditional interconnect material such as aluminum. In addition, diffusion between the aluminum and the surrounding insulating material often occurs, which adversely effects operation of the resulting electrical circuits.

Barrier materials have been introduced to improve both the step coverage and gap-fill of aluminum, while limiting diffusion of the same. Barrier materials must also provide good adhesion properties for aluminum. Otherwise, the thermal and electrical conductance of the resulting contact may be compromised. Examples of barrier materials providing the aforementioned characteristics include TiN, TiW, TiB₂, TiC and Ti₂N.

However, attempts have been made to provide interconnect material with lower electrical resistivity than aluminum. This has led to the substitution of copper aluminum. Copper, like aluminum, also suffers from diffusion characteristics and may form undesirable intermetallic alloys that reduce the availability of suitable barrier materials.

Tungsten has proved to be a suitable barrier material that effectively prevents diffusion of copper. Typically deposited employing chemical vapor deposition (CVD) techniques, tungsten deposition is attendant with several disadvantages. Tungsten diffuses easily into surrounding dielectric material. In addition, tungsten has proven difficult to deposit uniformly. This has been shown by variance in tungsten layers' thickness of greater than 1%. As result, it is difficult to control the resistivity of a tungsten layer.

What is needed, therefore, are improved techniques to form barrier layers for copper interconnects that include tungsten.

SUMMARY OF THE INVENTION

- 5 One embodiment of the present invention is directed to a method to form a stacked barrier layer on a substrate disposed in a processing chamber by serially exposing the substrate to first and second reactive gases to form an adhesion layer. The adhesion layer is then serially exposed to third and fourth reactive gases to form a barrier layer adjacent to the adhesion layer. A copper layer is disposed adjacent to the barrier layer.
- 10 To that end, another embodiment of the invention is directed to a system to carry out the method.

BRIEF DESCRIPTION OF THE DRAWINGS

- 15 Fig. 1 is a perspective view of a semiconductor processing system in accordance with the present invention;

Fig. 2 is a detailed view of the processing chambers shown above in Fig. 1;

Fig. 3 is a detailed cross-sectional view of a substrate shown above in Fig. 2 before deposition of a first refractory metal layer in accordance with one embodiment of the present invention;

- 20 Fig. 4 is a detailed cross-sectional view of the substrate shown above in Fig. 3 after deposition of a first refractory metal layer in accordance with one embodiment of the present invention;

- Fig. 5 is a detailed cross-sectional view of a substrate shown above in Fig. 4 after deposition of a second refractory metal layer in accordance with one embodiment of the present invention;
- 25

Fig. 6 is a detailed cross-sectional view of a substrate shown above in Fig. 2 after deposition of a copper contact in accordance with one embodiment of the present invention;

- 30 Fig. 7 is a schematic view showing deposition of a first molecule onto a substrate during sequential deposition techniques in accordance with one embodiment of the present invention;

Fig. 8 is a schematic view showing deposition of second molecule onto a substrate during sequential deposition techniques in accordance with one embodiment of the present invention;

Fig. 9 is a graphical representation showing the concentration of gases introduced into the processing chamber shown above in Fig. 2, and the time in which the gases are present in the processing chamber to deposit the Titanium refractory metal layer shown above in Fig. 4, in accordance with one embodiment of the present invention; and

Fig. 10 is a graphical representation showing the concentration of gases introduced into the processing chamber shown above in Fig. 2, and the time in which the gases are present in the processing chamber to deposit the Tungsten layer shown above in Fig. 4, in accordance with one embodiment of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

Referring to Fig. 1, an exemplary wafer processing system includes one or more processing chambers 12, 13 and 14 disposed in a common work area 16 surrounded by a wall 18. Processing chambers 12 and 14 are in data communication with a controller 22 that is connected to one or more monitors, shown as 24 and 26. Monitors 24 and 26 typically display common information concerning the process associated with the processing chambers 12 and 14. Monitor 26 is mounted to the wall 18, with monitor 24 being disposed in the work area 16. Operational control of processing chambers 12 and 14 may be achieved with use of a light pen, associated with one of monitors 24 and 26, to communicate with controller 22. For example, a light pen 28a is associated with monitor 24 and facilitates communication with the controller 22 through monitor 24. A light pen 28b facilitates communication with controller 22 through monitor 26.

Referring both the to Figs. 1 and 2, each of processing chambers 12 and 14 includes a housing 30 having a base wall 32, a cover 34, disposed opposite to the base wall 32, and a sidewall 36, extending therebetween. Housing 30 defines a chamber 37, and a pedestal 38 is disposed within processing chamber 37 to support a substrate 42, such as a semiconductor wafer. Pedestal 38 may be mounted to move between the cover 34 and base wall 32, using a displacement mechanism (not shown), but is typically fixed proximate to bottom wall 32. Supplies of processing gases 39a, 39b, 39c, 39d and 39e are in fluid communication with the processing chamber 37 via a showerhead 40. Regulation of the flow of gases from supplies 39a, 39b and 39c is effectuated via flow valves 41.

Depending on the specific process, substrate 42 may be heated to a desired temperature prior to layer deposition via a heater embedded within pedestal 38. For example, pedestal 38 may be resistively heated by applying an electric current from an AC power supply 43 to a heater element 44. Substrate 42 is, in turn, heated by pedestal 38, and can be maintained within a desired process temperature range of, for example, about 20 °C to about 750 °C, with the actual temperature varying dependent upon the gases employed and the topography of the surface upon which deposition is to occur. A temperature sensor 46, such as a thermocouple, is also embedded in the wafer support pedestal 38 to monitor the temperature of the pedestal 38 in a conventional manner. For example, the measured temperature may be used in a feedback loop to control the electrical current applied to heater element 44 by the power supply 43, such that the wafer temperature can be maintained or controlled at a desired temperature that is suitable for the particular process application. Pedestal 38 is optionally heated using radiant heat (not shown). A vacuum pump 48 is used to evacuate processing chamber 37 and to help maintain the proper gas flows and pressure inside processing chamber 37.

Referring to Figs. 1 and 3, one or both of processing chambers 12 and 14, discussed above may operate to form, on substrate 42, a contact in accordance with the present invention on substrate 42. To that end, substrate 42 includes a wafer 50 that may be formed from any material suitable for semiconductor processing, such as silicon. One or more layers, shown as layer 52, may be present on wafer 50. Layer 52 may be formed from any suitable material, including dielectric or conductive materials. Layer 52 includes a void 54, exposing a region 56 of substrate 42.

Referring to Fig. 4, formed adjacent to layer 52 and region 54 is a layer containing a refractory metal compound, such as titanium. In the present example, layer 58 is formed from titanium nitride, TiN, by sequentially exposing substrate 42 to processing gases to chemisorb monolayers of differing compounds onto the substrate, discussed more fully below. Layer 58 conforms to the profile of the void 54 so as to cover region 56 and layer 52.

Referring to Fig. 5, adjacent to layer 58 is formed an additional refractory metal layer 60. In the present example, layer 60 is formed from tungsten in the manner discussed above with respect to layer 52, except using different process gases. Layer 60 conforms to the profile of layer 58 and, therefore, conforms to the profile of void 54.

Referring to Fig. 6, shown is one example of a contact 62 formed in void 54 in accordance with the present invention by deposition of a layer of copper 64 that fills

void 54, using standard deposition techniques. With this configuration, a stacked barrier layer consisting of TiN layer 58 and W layer 60 surrounds contact 62. TiN layer 58 serves as an adhesion layer to facilitate nucleation and deposition by W layer 60. TiN layer also serves as a diffusion barrier to reduce, if not prevent, diffusion of W into the surrounding environs, such as region 56 and layer 52. W layer 60 serves as a barrier layer for contact 62, thereby preventing copper material from diffusing into or through TiN layer 58 and into the environs surrounding void 54. Employing sequential deposition techniques, such as atomic layer deposition, provides superior thermal and conductive characteristics of the aforementioned stacked barrier layer. Specifically, the sequential deposition techniques described below enable precise control over the thickness of both layers 58 and 60.

Referring to Figs. 1, 6 and 7, one or both of processing chambers 12 and 14, discussed above, may operate to deposit layers 58 and 60 on substrate 42 employing sequential deposition techniques. Specifically, the initial surface of substrate 42, e.g., the surface of region 56 and the surface of layer 52, presents an active ligand to the process region. A batch of a first processing gas, in this case Aa_x , results in a layer of A being deposited on substrate 42 having a surface of ligand x exposed to the processing chamber 37. Thereafter, a purge gas enters processing chamber 37 to purge the gas Aa_x . After purging gas Aa_x from processing chamber 37, a second batch of processing gas, Bb_y , is introduced into processing chamber 37. The a ligand present on the substrate surface reacts with the b ligand and B atom, releasing molecules ab and Ba, that move away from substrate 42 and are subsequently pumped from processing chamber 37. In this manner, a surface comprising a monolayer of A atoms remains upon substrate 42 and exposed to processing chamber 37, shown in Fig. 4. The process proceeds cycle after cycle, until the desired thickness is achieved.

Referring to both Figs. 2 and 8, although any type of processing gas may be employed, in the present example, the processing gas Aa_x is a titanium-containing gas selected from the group that includes TDMAT, TDEAT and $TiCl_4$. The processing gas Bb_y functions as a reducing agent and is selected from the group including H_2 , B_2H_6 , SiH_4 and NH_3 . Two purge gases were employed: Ar and N_2 . Each of the processing gases is flowed into processing chamber 37 with a carrier gas, which in this example, is one of the purge gases. It should be understood, however, that the purge gas may differ from the carrier gas, discussed more fully below. One cycle of the sequential deposition technique in accordance with the present invention includes flowing a purge gas into processing

chamber 37 during time t_1 before the titanium-containing gas is flowed into processing chamber 37. During time t_2 , the titanium-containing processing gas is flowed into the processing chamber 37, along with a carrier gas. After t_2 has lapsed, the flow of titanium-containing gas terminates and the flow of the carrier gas continues during time t_3 , purging the processing chamber of the titanium-containing processing gas. During time t_4 , the processing chamber 37 is pumped so as to remove all gases. After pumping of process chamber 37, a carrier gas is introduced during time t_5 , after which time the reducing process gas is introduced into the processing chamber 37 along with the carrier gas, during time t_6 . The flow of the reducing process gas into processing chamber 37 is subsequently terminated. After the flow of reducing process gas into processing chamber 37 terminates, the flow of carrier gas continues, during time t_7 . Thereafter, processing chamber 37 is pumped so as to remove all gases therein, during time t_8 , thereby concluding one cycle of the sequential deposition technique in accordance with the present invention. The aforementioned cycle is repeated multiple times until layer 58 reaches a desired thickness. After TiN layer 58 reaches a desired thickness, W layer 60 is deposited adjacent thereto employing sequential deposition techniques.

Referring to Fig. 2 and 10 to form W layer 60, processing gas Aa, may be any known tungsten-containing gas, such as tungsten hexafluoride, WF_6 . The processing gas Bb, functions as a reducing agent and is selected from the group including SiH_4 , B_2H_6 and NH_3 . The same purge gases may be employed, as discussed above. Each of the processing gases is flowed into the processing chamber 37 with a carrier gas, as discussed above. One cycle of the sequential deposition technique to form W layer 60 in accordance with the present invention includes flowing a purge gas into the processing chamber 37 during time t_9 , before the tungsten-containing gas is flowed into the processing chamber 37. During time t_{10} , the tungsten-containing processing gas is flowed into the processing chamber 37, along with a carrier gas. After time t_{10} has lapsed, the flow of tungsten-containing gas terminates and the flow of the carrier gas continues during time t_{11} , purging the processing chamber of the tungsten-containing processing gas. During time t_{12} , processing chamber 37 is pumped so as to remove all gases. After pumping of the process chamber 37, a carrier gas is introduced during time t_{13} , after which time the reducing process gas is introduced into the processing chamber 37 along with the carrier gas, during time t_{14} . The flow of the reducing process gas into processing chamber 37 is subsequently terminated. After the flow of reducing process gas into the processing chamber 37 terminates, the flow of carrier continues during time t_{15} .

Thereafter, the processing chamber 37 is pumped so as to remove all gases therein, during time t_{16} , thereby concluding one cycle of the sequential deposition technique in accordance with the present invention. The aforementioned cycle is repeated multiple times until layer 60 reaches a desired thickness. After W layer 60 reaches a desired thickness, the contact 62, shown in Fig. 6 may be deposited employing known techniques.

The benefits of employing sequential deposition are manifold, including flux-independence of layer formation that provides uniformity of deposition independent of the size of a substrate. For example, the measured difference of the layer uniformity and thickness measured between of 200 mm substrate and a 32 mm substrate deposited in the same chamber is negligible. This is due to the self-limiting characteristics of chemisorption. Further, the chemisorption characteristics contribute to near-perfect step coverage over complex topography.

In addition, the thickness of the layers 58 and 60 may be easily controlled while minimizing the resistance of the same by employing sequential deposition techniques. In one example of the present invention, layers 58 and 60, as well as contact 62 may be deposited in a common processing chamber, for example chambers 12 and 14. To provide added flexibility when depositing layers 58 and 60, as well as contact 62, a bifurcated deposition process may be practiced in which layer 58 is deposited in one process chamber, for example chamber 12, and layer 60 is deposited in a separate chamber, for example chamber 14. This may reduce the deposition time of each of layers 58 and 60 by, *inter alia*, having each processing chamber 12 and 14 preset to carry-out the process parameters necessary to deposit the requisite refractory metal layers.

Referring again to Fig. 2, the process for depositing the tungsten layer may be controlled using a computer program product that is executed by the controller 22. To that end, the controller 22 includes a central processing unit (CPU) 70, a volatile memory, such as a random access memory (RAM) 72 and permanent storage media, such as a floppy disk drive for use with a floppy diskette, or hard disk drive 74. The computer program code can be written in any conventional computer readable programming language; for example, 68000 assembly language, C, C++, Pascal, Fortran, and the like. Suitable program code is entered into a single file, or multiple files, using a conventional text editor and stored or embodied in a computer-readable medium, such as the hard disk drive 74. If the entered code text is in a high level language, the code is compiled and the resultant compiler code is then linked with an object code of precompiled Windows® library routines. To execute the linked and compiled object code the system user invokes

the object code, causing the CPU 70 to load the code in RAM 72. The CPU 70 then reads and executes the code to perform the tasks identified in the program.

- Although the invention has been described in terms of specific embodiments, one skilled in the art will recognize that various changes to the reaction conditions, i.e., temperature, pressure, film thickness and the like can be substituted and are meant to be included herein and sequence of gases being deposited. For example, sequential deposition process may have different initial sequence. The initial sequence may include exposing the substrate the reducing gas before the metal-containing gas is introduced into the processing chamber. In addition, other stacked layers may be deposited, in addition to the refractory-metal layers described above and for purposes other than formation of a barrier layer. Tungsten and other deposition techniques may be employed in lieu of CVD. For example, physical vapor deposition (PVD) techniques, or a combination of both CVD and PVD techniques, may be employed. Therefore, the scope of the invention should not be based upon the foregoing description. Rather, the scope of the invention should be determined based upon the claims recited herein, including the full scope of equivalents thereof.

00005609-052001